EFFECT OF MERCURY CONCENTRATION AND OPERATING PARAMETERS TO MERCURY REMOVAL USING PORTABLE MERCURY REMOVAL RIG (PMRR) FOR PETROCHEMICAL WASTEWATER

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ABSTRACT

Mercury is a type of heavy metal that naturally occurs on the earth crust. It can be found in soil, rocks and sea. It can be release to the environment through natural processes such as rock erosion, soil decomposition or volcanoes eruptions. It also released to the environment by human activities such as mining and industrial processes from petrochemical and chlor-alkali industries. Mercury is usually used in the thermometer, thermostat, barometer, bulbs, dental amalgams and switches. Mercury is one of the hazardous chemical elements that exist on the earth. It can attack human central nervous system, kidney, lungs and other body systems. Thus the objective of this research is to study on the mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR) for petrochemical wastewater. The mercury removal process was conducted under different inlet pressure; 5, 10 and 23 psig, different inlet concentration; 2, 4, 6 and 8 ppm, different pH and lastly using different absorbent; extruded activated carbon (EAC), granular activated carbon (GAC) and ion exchange (IE) resins. As the result, the best inlet pressure was 5 psig while the best inlet concentration is from 2-4 ppm. The best absorbent is ion exchange because of faster mercury removal mechanism while low pH is preferred for operating parameter of PMRR. As the conclusion, the mercury removal is increased as the pressure, inlet concentration and pH value are decreased.

KESAN KEPEKATAN MERKURI DAN OPERASI PARAMETER KEPADA PENYINGKIRAN MERKURI MENGGUNAKAN ALAT PENYINGKIR MERKURI MUDAH ALIH (PMRR) BAGI AIR SISA PETROKIMIA

ABSTRAK

Merkuri adalah sejenis logam berat yang secara semulajadi wujud pada kerak bumi. Ia boleh didapati di dalam tanah, batu-batu dan laut. Ia boleh dilepaskan ke persekitaran melalui proses semula jadi seperti hakisan batu, penguraian tanah atau letusan gunung berapi. Ia juga dilepaskan kepada alam sekitar oleh aktiviti manusia seperti perlombongan dan proses perindustrian daripada petrokimia dan industri klor-alkali. Merkuri biasanya digunakan dalam termometer, termostat, barometer, mentol, amalgams gigi dan suis. Merkuri adalah salah satu daripada unsur-unsur kimia berbahaya yang wujud di muka bumi. Ia boleh menyerang pusat sistem saraf manusia, buah pinggang, paru-paru dan sistem badan yang lain. Oleh itu, objektif kajian ini adalah untuk mengkaji kandungan merkuri dan parameter operasi untuk membuang merkuri menggunakan Alat Penyingkir Merkuri Mudah Alih (PMRR) untuk air sisa petrokimia. Proses penyingkiran merkuri telah dijalankan di bawah tekanan masuk yang berbeza; 5, 10 dan 23 psig, kandungan merkuri pada aliran masuk yang berbeza, 2, 4, 6 dan 8 ppm, pH yang berbeza dan akhir sekali menggunakan penyerap berbeza; karbon aktif mampat, karbon aktif berbutir dan resin pertukaran ion. Hasilnya, tekanan masuk terbaik adalah 5 psig manakala kepekatan aliran masuk yang terbaik adalah 2-4 ppm. Penyerap terbaik adalah pertukaran ion kerana kepantasan mekanisma pembuangan merkuri manakala pH rendah lebih sesuai untuk parameter operasi PMRR. Sebagai kesimpulan, penyingkiran merkuri meningkat kerana tekanan, kepekatan masuk dan nilai pH menurun.

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LIST OF SYMBOLS

Hg	Mercury
Xe	Xenon
˚C	Degree Celsius
µg/L	Microgram per litre
mg/L	Milligram per litre
µg/kg	Microgram per kilogram
ppm	Parts per million
mL	Millilitre
g	Gram
%	Percent
L	Litre
psig	Pounds per square inch gauge
psi	Pounds per square inch

LIST OF ABBREVIATIONS

DOE	Department of Environment
PMRR	Portable Mercury Removal Rig
FAO	Food and Agriculture Organization
PTWI	Provisional Tolerated Weekly Intake
COD	Chemical Oxygen Demand
EAC	Extruded activated carbon
GAC	Granular activated carbon
IE	Ion exchange
BOD	Biochemical Oxygen Demand

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Mercury is one of a very hazardous chemical element that exists on the earth. It is a naturally occurring element and can be found in soil, rock and ocean. It can be released to the environment by volcanoes eruption, rocks erosions and soil decomposition. With chemical symbol of Hg, mercury is located in group 12 and period 6 in the periodic table. It is also located under d-block in the periodic table with electron configuration of [Xe] $4f^{14}5d^{10}$ $6s^2$. Having an atomic number of 80, it is a transition metal that is silver in colour and also called quicksilver or hydrargyrum. Mercury is the only metal that exists in liquid form under standard room temperature. It has melting point of -38.87°C and boiling point of 356.72°C (Risher, 2003). It does not react with most acid but dissolve in many metals such as gold, aluminium and zinc to form amalgams. Examples of metal that do not dissolve mercury include iron, platinum, tungsten and tantalum.

Mercury has been widely used thoroughly in the industries. It is used in the thermometer to measure the temperature. Besides, it is also used in the manometer and barometer, devices that are used in order to measure the pressure. Mercury amalgams are widely in dentistry by applying it on the teeth. Amalgams become dental restorative material choice because of it low in cost, easy for application, high strength and durable. Mercury is also used in batteries, normal fluorescent bulb and switch. But due to it carcinogenic effect, wide variety of choices and enhancement of nowadays technologies, their popularity has decreased.

1.2 Problem Statement

Mercury is one of heavy metal that flow through the wastewater of petrochemical industries. The problem of mercury in the wastewater not only is the concern of the company but also Department of Environment (DOE). Mercury exists in several forms that are elemental mercury, organic mercury and lastly inorganic mercury. Different type can cause different type of illness or hazards. Generally when mercury enters human body, they will attack the central nervous system and liver. Mercury can cause blindness, mental and emotional deterioration, involuntary immobilization and other. Mercury is also mutagenic, teratogenic, carcinogenic and promotes tyrosinemia.

The discharge limit value for mercury in wastewater is about 10 µg/ L and the limit standard value of mercury in drinking water is 2 µg/ L (Zhang et al., 2005). While in the common wastewater from petrochemical industries is about 0.1- 9 mg/ L. This value is way over from the permitted standard and wastewater treatment

should be done to remove the mercury before the wastewater can be discharged into the oceans. With such a high value human being that exposed to the water contaminated with mercury can be affected. One of the examples for disaster that is cause by mercury in the past is in the late 1950s when more than hundreds people are killed and disabled through the intake of fish and shellfish. This disaster was happened in Minamata, Japan.

Many technologies have been identified to be capable of removing mercury from wastewater. They are including several physical and chemical separation processes such as solvent-extraction, ion-exchanged, precipitation, membrane separation, reverse osmosis, coagulation, adsorption and activated carbon. Many researchers have found that adsorption is an effective way to remove mercury while activated carbon is very effective but it is expensive for large scale application. The other techniques stated required either high energy or big amount of chemicals. Furthermore, current technologies used require large space in plant or oil rig but by applying Portable Mercury Removal Rig (PMRR), this problem can be solved. Besides, the benefit of using is it requires fewer workers to operate the rig. Thus the company can save space and cost that can be used for other purposes.

1.3 Objective of Research

The objective of this research is to study the effect of mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR) for petrochemical wastewater.

1.4 Scope of Research

The objective of this research is to study the effect of mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR) for petrochemical wastewater.

Due to the objective is to remove mercury from petrochemical wastewater, thus several components must be studied on.

1. To determine the most influence parameter in mercury removal using PMRR.
2. To determine percentage of mercury removed after treated by PMRR.
3. To compare the quality of wastewater with the standard after it has been treated by PMRR.
4. To determine the most effective method of removing mercury from wastewater either by ion exchange or activated carbon.

1.5 Significances of Research

This research is significance because mercury is a highly toxic material and it can bring many bad effects to the human health. Petrochemical industries are important to Malaysia economy and it can affect many citizens because wastewater that flowing from this type of industry will go directly to the ocean. Mercury can enter the food chain from fish and the higher consumer in the food chain, the higher mercury contamination it can have. This will reflect to human because usually human will be the last consumer in the food chain. This research is also significance because of every wastewater to be released into the sea need to follow or satisfy

Department of Environment (DOE) requirements. Failing to follow the rules, the operation of the petrochemical company may force to stop and what worse is the aquatic ecosystem in the sea may endanger by action taken by the greedy company.

CHAPTER 2

LITERATURE REVIEW

Many have agreed that mercury is hazardous to living thing especially human. Human can consume mercury when they eat fish from the ocean. When mercury has entered the sea, microorganisms will convert the inorganic mercury into methylmercury. Fish then eat this microorganism that result the fish to be contaminated by mercury. Thus, human that consume the fish will also consume the methylmercury. What worsen the situation is methylmercury is more carcinogenic than inorganic mercury. Although inorganic mercury is less harm than methylmercury, Lloyd-Jones et al. (2004) state that high level exposure to inorganic mercury can permanently damage the brains, kidneys and foetus. Such concerns in this topic, many researchers have studied different method to remove mercury in the water. Due to this concern, this literature will review on the effect of mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR).

2.1 Sources of Mercury

Mercury is a natural occurring element that can be found in rocks, soil and ocean. It can be released into the environment by volcanoes eruption, rocks erosion and soil decomposition. Mercury is commonly used in temperature measurement tools such as thermometer and thermostat but it is also used in pressure measurement devices such as manometer and barometer. Manohar et al. (2002) state that wastewater that comes from industries such as chlor-alkali manufacturing, oil refinery, paint, pharmaceutical and battery manufacturing industries contain mercury. But out of all industries that have been stated, chlor-alkali manufacturing industries have been the main contributor for mercury contamination in environment said Mohan et al. (2001). People may be exposed to mercury from a variety of sources, including drinking water. Inorganic mercury compounds such as mercuric chloride are used in batteries, paper manufacturing and chemical industries. On the other hand, organic mercury compounds such as methyl mercury are found in large fish such as bass, shark, swordfish and tuna. In the past, mercury was used in indoor paints and agricultural pesticides and is used to prevent mildew in outdoor paints.

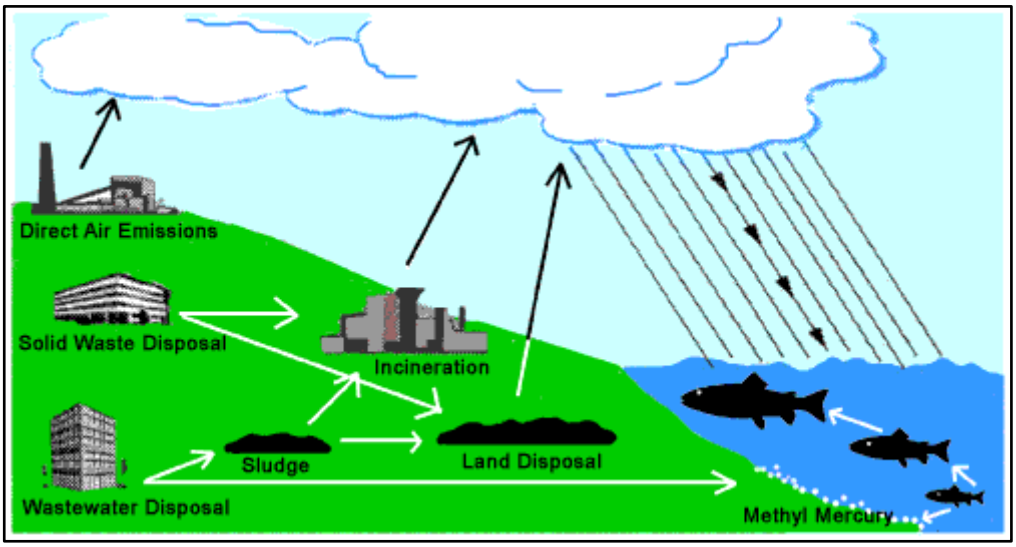

Figure 2.1 Sources of mercury released into the environment

2.2 Hazard that will come out as the Effect from Mercury Contamination

Mercury has been classified as one of the most hazardous element that can be found on the earth. Dabrowski et al. (2004) also agreed with this statement by stating in their research that mercury can spread easily in the environment and will be accumulated by living organisms. Many health effects can be cause by mercury contamination in human body such as brain and kidney damage. In the word of Manohar et al. (2002), high concentration of mercury in the body can cause damage to pulmonary function, chest pain and difficulty to breathe (dyspnoea). They also said that mercury can easily pass brain-blood barrier and damage the brain. Risher (2003) added that mercury also can cause cardiovascular effect, gastrointestinal effect, hepatic effect, irritation and sensitization, genotoxic effect and cancer. One of the examples for mercury hazard come in late 1950s as more than a hundred people life in Minamata bay, Japan were killed and disabled after they eating fish and shellfish that contaminated with methylmercury. Besides that, mercury can also bring negative effect to developing foetus when the mother is consuming foods that are contaminated by mercury. UN Food and Agriculture Organization (FAO) have suggested Provisional Tolerated Weekly Intake (PTWI) for methylmercury to be 1.6 µg/kg body weight in order to prevent the developing foetus be damaged (Malakahmad et al., 2011). According to Langford and Ferner (1999) the toxicity of mercury is different from elemental mercury metal, inorganic mercury salts and organometallic mercury compound. Inorganic mercury compounds are the most common forms of mercury found in drinking water. While organic mercury compounds are the most harmful forms of mercury are rarely found in drinking water.

2.3 Mercury in Drinking Water

Mercury carried by wind and rain is found throughout the environment mostly due to the release of naturally occurring mercury from rock and soil, burning of coal and oil that contains small amount of mercury, release of mercury from metal smelters and incineration of materials that contain mercury such as batteries. There are many ways that mercury can get into drinking water firstly by rain and snow can carry mercury from the air into surface water supplies such as lakes, rivers and reservoirs. Mercury also can seep into underground water supplies from industrial and hazardous waste sites. Improperly disposed household products such as mercury containing outdoor paints also contribute to the problem by moving through the soil and reach private well water supplies. In addition, past application of mercury-based pesticides on agricultural lands such as farm and fruit orchards can wash into nearby surface water or travel through the soil into underground water supplies can worsen the problem.

2.4 Methods to Remove Mercury from Water

There are many methods that can be used to remove mercury from water. Each of the method has their own advantages and disadvantages and the table below will show the results obtained by other researchers.

Table 2.1 Methods of mercury removal from water

Title of literature (authors, year)	Method of removing mercury	Result
Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste (Mohan et al.,2001)	Activated carbon	Adsorption of mercury increased with decrease in temperature and solution pH
Mercury removal from aqueous solutions by complexation ultrafiltration (Barron-Zambrano et al.,2002)	Complexation-ultrafiltation	In acidic medium the mercury retention strongly depends on pH
Mercury removal using a poly(vinylalcohol)/ poly(vinylimidazole) complexing membrane (Bessbousse et al.,2010)	Membrane	When used in the filtration mode, the elimination ratio of mercury was greater or equal to 99.4%
Mercury removal from water by ion exchange resins adsorption (Chiarle et al.,2000)	Ion exchange resins	Sorption capacity is very high and strongly dependent on the initial pH
Sequencing Batch Reactor (SBR) for the removal of Hg2+ and Cd2+ from synthetic petrochemical factory wastewater (Malakahmad et al.,2011)	Micoorganism in batch reactor	The treated wastewater will achieve considerable chemical oxygen demand (COD)
Mercury (II) removal from water by electrocoagulation using aluminium and iron electrodes (Nanseu-Njiki et al.,2009)	Electrocoagulation	More than 99% of pollutant was eliminated and removal efficiencies do not vary significantly on type of electrode.

2.5 Important Operating Parameters in Order to Remove Mercury from Wastewater

Many operating parameters can be assumed to be important to remove mercury from wastewater. From Chiarle et al. (2000), they have stated that the lower the initial pH, the lower the concentration of mercury at the uptake. Thus, the pH of the water can be related to the concentration of mercury at the inlet of PMRR. Besides, the pressure of the PMRR during the treatment process can also have the effect on the efficiency of the adsorption process. The pressure in the PMRR can affect the flow rate of the wastewater containing the mercury. It has been proved that the pressure in the PMRR is directly proportional to the flow rate of the wastewater enter the PMRR from the dilution tank. When the flow rate of wastewater is high, thus the water cannot be treated in a proper time and as the result, the mercury is less efficient to be removed from the wastewater.

2.6 Advantages of using PMRR for Mercury Removal

The current system that is used at the petrochemical industries to remove mercury from their wastewater is requiring large space. Thus by applying PMRR at the petrochemical industries, much space can be saved and used for other things. Secondly, PMRR does not require many workers, thus the company can saved more money. The system used in PMRR is just simple and only need one or two workers. Thirdly, PMRR is easily to move around the workplace. From this advantage, many section of the company can used the same PMRR without adding other piping to connect several sections in order to remove mercury from the wastewater. The

system that currently applied to PMRR is quiet easy thus workers assigned to operate the rig do not require high training as well as the rig is really safe to operate. Now it has been proved although PMRR is just a small system, but it can challenge the current system that used to remove mercury in the petrochemical wastewater.

2.7 Ion Exchange Resins

Rengaraj and Moon (2002) state the removal of heavy metal pollutants at high concentrations from water can be readily accomplished by chemical precipitation or electrochemical method. They also state the removal for low concentrations heavy metal is more effective if implemented by ion exchange or adsorption on solid sorbent such as activated carbon as supported by Sigworth and Smith (1972). For this experiment, Lewatit® MonoPlus TP 214 ion exchange resins are selected to be used. This type of ion exchange is monospherical, and having a high affinity for mercury. It has a good capacity for platinum metals, gold and silver and specially used to remove mercury from flue gas and ground water. This resin offers higher mechanical and osmotic stability, better kinetics, higher capacity and remarkable low leakage according to the process conditions.

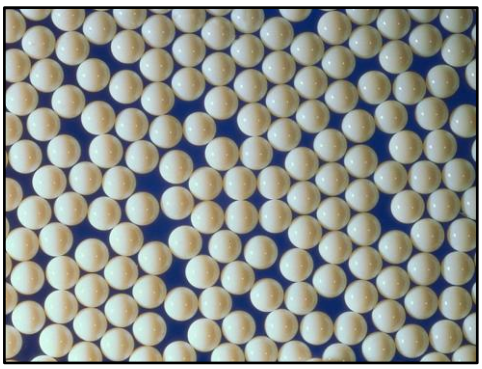

Figure 2.2 Ion exchange resins

2.8 Activated Carbon

Activated carbon can be produced from a variety of carbonaceous raw materials, by either a physical or chemical activation methods. The adsorptive capacity of the final product depends on internal surface area, pore structure and surface chemistry that are defined by the nature of the starting material and production process. According to Skodras et al. (2007), among air pollution control applications, carbon-based processes including both direct injection and fixed bed have been developed for mercury uptake from municipal and hazardous waste incinerators. Yardim et al. (2003) said activated carbons are widely used as adsorbents for removing different pollutants from drinking water. This shows that activated carbon or also known as activated charcoal is commonly used in water purification system. In recent years, activated carbon is derived or prepared from various cheaper and alternative materials such as agricultural by-product and waste of polymer materials thus reducing its cost and can be used in large scale application compared to ion exchange.

Figure 2.3 Activated carbon as solid sorbent in water purification method

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this study, there are several steps that need to be conducted before the experiment, during the experiment and after the experiment. In this chapter, the steps will clearly explained in their section respectively such as the set up for Portable Mercury Removal Rig (PMRR), the installation of absorbent, the preparation for the synthetic mercury wastewater and mercury analysis preparation.

3.2 Research Design

This research is a qualitative research thus it will focus on the concentration of mercury in the water at the outlet of the PMRR. This research proposes to study on the effect of mercury concentration and operating parameters for mercury removal using PMRR. Thus the operating parameters such as temperature, pressure and pH

value also will be investigated to know on how it will affect the mercury concentration that will be removed during the process. At the end, the mercury concentration in the water will be analyzed to make sure whether the PMRR is effective in removing mercury from water or not.

Figure 3.1 Portable Mercury Removal Rig (PMRR)

3.3 Procedures before the Experiment

3.3.1 To prepare stock solution

In this experiment, 1000 ppm of mercury stock solution was prepared before diluted for the purpose of the experiment. Several apparatus were needed to prepare the stock solution such as weighing boat, electronic balance, spatula, 500 mL volumetric flask, dropper, glass rod and beaker. Materials used to prepare stock were